(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 177 730**
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **85110728.4**

(22) Date of filing: **27.08.85**

(51) Int. Cl.⁴: **C 08 F 283/10**, C 09 D 3/00

(30) Priority: **21.09.84 US 652858**

(43) Date of publication of application: **16.04.86**
Bulletin 86/16

(84) Designated Contracting States: **BE DE FR GB IT NL**

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(54) Epoxy graft acrylic water-based primer surfacers.

(57) Dispersion of an epoxy ester graft acrylic in water with a total of no more than 5% of organic volatiles and amines. These dispersions can be used in primer compositions for metal substrates having a minimum of organic solvent emissions and which can crosslink at temperatures from 140–200 °C, giving a good balance of hardness, flexibility, humidity, corrosion resistance and anti-chipping properties.

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TITLE

Epoxy Graft Acrylic Water-Based Primer Surfaces

BACKGROUND

This invention relates to epoxy ester polymers having acrylic portions grafted thereto. More particularly, it relates to coating compositions containing such polymers.

U.S. Patent 4,302,373 - Steinmetz (Nov. 24, 1981) describes water-borne coating compositions of epoxy resin, polymeric acid and tertiary amine, wherein the epoxy functionality is partially capped with a carboxylic acid polymer to form a hydrogel. Coating compositions made therefrom are taught for use in can coatings and for automotive and paper coatings.

An acetic acid-neutralized aqueous polyaminoamido resin made using dimeric fatty acids is disclosed in European Patent Application Publication 60581 of September 22, 1982 - Guenter et al (Akzo).

Other aqueous epoxy coating compositions also outside the present invention are disclosed in U.S. Patents

4,446,258 of May 1, 1984 - Chu et al (Mobil Oil),

4,446,260 of May 1, 1984 - Woods et al (International Paint), and

4,444,806 of April 24, 1984 - Morgan et al (W. R. Grace).

SUMMARY OF THE INVENTION

The present invention provides a dispersion in water, in percentages by weight based on the total dispersion, of:

(a) 10-60% of an epoxy ester graft acrylic polymer formed by reacting 5-30% of an epoxy ester polymer formed by reaction of n moles of a difunctional epoxy resin with terminal oxirane groups and a number average molecular weight ($\overline{Mn}$) of 300-5000, n-1 moles of a diacid, and 2 moles of a monofunctional acid to form a reaction product, onto which is grafted 5-30% of an acrylic monomer by using a peroxide or azo initiator, to produce said epoxy ester acrylic polymer with a $\overline{Mn}$ = 1000-50,000 and an acid number of 30-150,

(b) tertiary amines being added to an extent equivalent to neutralizing 50-200% of the moles of acid functionality,

(c) organic solvents,

such dispersion having not more than 10% volatile organic solvents plus amines, and

(d) balance water.

The epoxy ester graft acrylic polymers of (a) above, and methods of making them, are also subject matters of the invention.

DETAILED DESCRIPTION

The present invention is made possible by a new method of synthesis of an epoxy ester graft acrylic polymer. The process involves the synthesis of a linear epoxy ester formed by reaction at 80-190°C of an oxirane terminated bisphenol A epoxy resin with aliphatic diacids and monoacids in approximately stoichiometric proportions so that

all the oxirane groups and acid groups have reacted. The reaction is done in a minimum amount of an organic solvent, preferably aromatic for ease of stripping, preferably using a small percentage of a tertiary amine as catalyst. In a second stage an acid functional acrylic is grafted onto the epoxy ester using a peroxide or azo initiator. Grafting onto the epoxy ester is believed to go via hydrogen abstraction of activited carbon-hydrogen bonds. In a third stage the acid functionality on the epoxy ester is neutralized with a tertiary amine (50-200% neutralization), the polymer is dispersed in deionized water the excess organic solvents are distilled off. Thus, the epoxy ester and acrylic graft are formed in an aromatic solvent, neutralized with the amine and the aromatic solvent distilled off.

These epoxy ester-acrylic dispersions then contain a minimum of organic solvents, so as to be able to formulate primer compositions, preferably with no more than 5% organic volatiles. The dispersions can contain 0 to 10% of a water soluble organic solvent.

When combined with water soluble or dispersible crosslinkers, like hexamethoxymethylmelamine, pigments and extenders, primer surfacers can be formulated which show good corrosion resistance over bare steel, an excellent balance of hardness, flexibility, anti-chipping properties, good topcoat hold-out and appearance.

These primer surfacers can be baked for 30 min at from 160°C to 200°C, still retaining their basic properties. The primers can be applied by conventional or electrostatic spraying. To further improve application and flow properties, rheology control agents and flow agents can be used. Silica or clay pastes are quite successful for rheology control to prevent pinholing and

sagging, and water soluble or dispersable linear or branched polyethylene glycols or polypropylene-glycols are efficient for flow properties. The primer surfacers show excellent initial and wet adhesion over bare steel and cathodic electrodeposited primers. Adhesion and hold-out of conventional topcoats (polyester, alkyd, acrylic) is very good over broad temperature ranges. Hold-out is the resistance to interpenetration at the interface between the layers of primer surfacer and topcoat applied in organic solvents.

The following are examples describing manufacture of epoxy ester graft acrylic dispersions. Parts, proportions and percentages are by weight except where indicated otherwise.

EXAMPLE 1

Ingredient	Parts	Producer
Xylene	2.73	
Pripol 1014 dimerized fatty acid (Pri)	2.80	Unichema
Epon 1001 epoxy resin	9.62	Shell
Dimethylolpropionic acid (DMPA)	1.304	
Dimethylcyclohexylamine (DMCA)	0.032	

Heat at reflux for 3 hours until acid number (AN) is below 3.

Xylene	1.00	

Heat at reflux 150-155°C while adding over 30 min keeping the exotherm under control.

Styrene (S)	2.194	
Methylmethacrylate (MMA)	2.572	
Butylacrylate (BA)	5.039	
Hydroxyethylacrylate (HEA)	0.718	
Acrylic acid (AA)	0.824	

Trigonox C tert-butylperoxy-benxoate (BPB)	0.128	Akzo
Xylene	0.583	
Mercaptoethanol	0.200	
Add over 30 min, hold 10 min.		
Xylene	1.747	
S	2.95	
MMA	2.572	
BA	1.137	
HEA	0.93	
AA	1.648	
BPB	0.384	
Mercaptoethanol	0.60	
Add over 90 min, hold 2 hours.		
Cool down to 90°C.		
Dimethylethanolamine (DMEA)	3.113	
Deionized water (DW)	0.911	
Add - mix 15 min.		
DW	10.06	
Add and heat at reflux, about 100°C.		
DW	49.89	

Add slowly while distilling off all organics insoluble in DW at reflux.

Test results: solids 37% (measured 2 hours at 125°C)
Brookfield viscosity measured at 20 RPM 9800 centipoises (cps) = 9800 milliPascal seconds (mPas)
pH 7.75

EXAMPLE 2

Ingredient	Parts
Epon 1001	6.59
Pri	19.17
DMPA	0.893
DMCA	0.023
Cellosolve acetate	0.577
Xylene	0.60
Heat at 150-160°C until AN below 3.	
Xylene	1
Add and bring to reflux	
S	3.525
MMA	3.525
BA	4.23
HEA	1.128
AA	1.692
BPB	0.35
Mercaptoethanol	0.55
Xylene	0.80
Add over 2 hours. Reflux 2 hours.	
DMEA	1.269
DW	1.731
Add. Mix 15 min.	
DW	33.519

Add 30%, mix, then add remaining 70% while stripping off organics insoluble in DW.

Test results: solids 32%
visc. 8000 mPas
pH 8.1

EXAMPLE 3

Xylene	1.74	
Epon 828 epoxy resin	6.13	Shell
Pri	5.18	
DMPA	2.414	
DMCA	0.032	
Heat at reflux until AN ≤ 3.		
Xylene	0.50	
Heat at reflux		
S	2.792	
MMA	2.572	
BA	5.039	
HEA	0.718	
AA	0.824	
BPB	0.128	
Xylene	0.683	
Mercaptoethanol	0.100	
Add over 30 min, hold 10 min.		
Xylene	1.747	
S	2.95	
MMA	2.572	
BA	1.137	
HEA	0.930	
AA	1.648	
BPB	0.384	
Mercaptoethanol	0.300	
Add over 90 min, hold 2 hours.		
DMEA	3.113	
DW	0.911	
Add, mix 15 min.		
DW	10.06	

Add and strip off organic volatiles, then add:

DW		49.89
Test results:	solids	30.5
	pH	7.8
	visc.	9400 cps

EXAMPLE 4

Xylene	2.75
Pri	2.80
Epon 1001	9.62
DMPA	1.304
DMCA	0.032

Heat at reflux for 3 hours until AN ≤3.

2 Ethylhexanol	8
S	1.235
BA	5.311
AA	0.988
HEA	0.618
Methanol	1.30

Add and heat at reflux ± 100°C.

Lucidol benzoylperoxide	0.07	AKZO
MMA	3.952	
Mercaptoethanol	0.05	
2-ethylhexanol	0.70	

Add, hold 10 min.

MMA	4.694
S	0.824
BA	0.865
HEA	0.617
AA	1.482
Benzoylperoxide	0.35

Add 30% over 15 min.

Add 45% over 50 min.

Add 25% over 80 min.

Hold 30 min.

DMEA 3.053

Add, mix 15 min.

DW 65.69

Add while stripping off organics insoluble in DW.

Test results: solids 32.1%
visc. 800 cps mPas
pH 7.8

Following are examples describing manufacture of primer surfacer paints or finishes with a content of organic volatiles of no more than 5%.

Following are examples describing manufacture of finishes paints, application and properties:

EXAMPLE 5

Resin dispersion of Example 2	60.93	
DW	6.08	
DMEA	0.29	
Surfynol 104 E anti-form/ anti-cratering agent	1.84	Air Products
Pluriol P 900 polypropylene oxide mol. sgt. 900 (reactive diluent)	2.26	BASF
Cymel 303 hexamethoxymethylmelamine	4.20	Cyanamid
Aerosil 200 fumed silica	0.87	Degussa
Blanc Fixe barium sulfate	10.13	Sachtleben
Aluminum silicate	2.56	
Titanium dioxide pigment	6.73	
Carbon black	0.034	

Iron oxide	0.145
Deionized water	3.941
	100.000

Pigment to binder ratio (P/B) = 74.3 / 100
Binder ratio: 76.5/15.3/8.2: Resin of Example 2/ Cymel 303/Pluriol P 900.

The above mixture is ground to a fineness smaller than 15 µm. Next there is added deionized water to obtain a package viscosity of 100 to 150 sec DIN cup 4 at 20°C.

EXAMPLE 6

The procedure of Example 5 was repeated with the exception that the resin dispersion of Example 2 was replaced by resin of Example 1.

EXAMPLE 7

The procedure of Example 5 was repeated with the exception that the melamine resin Cymel 303 was replaced by Cymel 350, another melamine resin.

EXAMPLE 8

The procedure of Example 5 was repeated with the exception that the dimethylethanolamine was replaced by DMAMP 80 (2-dimethylamino-2-methyl-1-propanol) from IMC Co.

EXAMPLE 9

The procedure of Example 5 was repeated with the exception that reactive diluent Pluriol P 900 (polypropylene oxide, molecular weight 900) was replaced by Luphen 1320 from BASF (branched polyethyleneglycol).

EXAMPLE 10

The procedure of Example 5 was repeated with the exception that Aerosil 200 was replaced by Bentone EW bentonite clay from NL Chemicals.

EXAMPLE 11

The procedure of Example 5 was repeated with the exception that the P:B ratio was changed from 74.3/100 to 50/100.

PANEL PREPARATION

The products of Examples 5-11 were reduced with deionized water to a spray viscosity of 20 seconds DIN cup 4 at 20°C. The coating composition obtained was sprayed over a cataphoretic electrocoated panel at a thickness of 35 µm dry film thickness and cured at a temperature of 170°C for 25 minutes.

The obtained primer film was coated with different topcoats including alkyd/melamine/acrylic/melamine color coat - clear coat resulting in excellent adhesion gloss, flow and DOI. Test results on the coating properties are given in Table I in terms of:

- Buckholz hardness : DIN 53153
- Erichson flexibility : DIN 53156
- Salt spray : DIN 50021. The rust creepage from the scribeline is measured in mm.

All Examples were submitted to the humidity cabinet according to DIN 50017 for 240 hours over bare steel and 480 hours over electrocoated panels. In neither of the tests did any blistering occur. Good chip resistance was also observed.

TABLE I

Example No.	Buchholz Hardness	Erichson Flexibility	Salt spray over electrocated panel 500 hrs	Salt spray over bare steel 144 hrs
5	98.0	5.9 mm	0 mm	3 mm
6	85.0	6.5 mm	0 mm	5 mm
7	133.0	4.4 mm	0 mm	7 mm
8	100.0	5.4 mm	0 mm	6 mm
9	107.0	5.5 mm	0 mm	2 mm
10	100.0	5.2 mm	0 mm	4 mm
11	92.0	6.5 mm	0 mm	4 mm

CLAIMS

1. A dispersion in water of:

(a) 10-60% of an epoxy ester graft acrylic polymer formed by reacting 5-30% of an epoxy ester polymer formed by reaction of n moles of a difunctional epoxy resin with terminal oxirane groups and a number average molecular weight ($\overline{Mn}$) of 300-5,000, n-1 moles of a diacid, and 2 moles of a monofunctional acid to form a reaction product, onto which is grafted 5-30% of an acrylic monomer by using a peroxide or azo initiator, to produce said epoxy ester acrylic polymer with a $\overline{Mn}$ = 1000-50,000 and an acid number of 30-150,

(b) tertiary amines being added to an extant equivalent to neutralizing 50-200% of the moles of acid functionality,

(c) organic solvents,

such dispersion having not more than 10% volatile organic solvents plus amines, and

(d) balance water.

2. The dispersion of claim 1 with 5-20% epoxy ester and 10-30% of an acrylic with acid number 60-140 in 50-80% deionized water, having been azeotropically distilled to leave not more than 5% organic volatiles.

3. The dispersion of claim 1 with the epoxy ester formed by reaction of n moles of a difunctional bisphenol A-based epoxy with $\overline{Mn}$ = 300-2000, n-1 moles an aliphatic-based difunctional acid with a total of 4-40 carbon atoms and 2 moles of monofunctional acid having 2-25 carbon atoms.

4. The dispersion of claim 1 with the acrylic graft formed by reaction of alkyl acrylate, alkyl methacrylate, styrene, hydroxyfunctional acrylates and/or methacrylates, acid functional acrylates and/or methacrylates, alkylmaleates and/or fumarates, using 0.01-10% by weight of initiator based on the acrylic content, at 60-180°C, with the acrylic having an acid number of 40-120.

5. The dispersion of claim 1 with the epoxy ester-graft acrylic having been neutralized with a tertiary amine which has a boiling point of 60-220°C.

6. The dispersion of claim 1 of which at least 5-15% is epoxy ester, 5-15% is acrylic graft, up to 5% is neutralizing amine plus organic solvent, and 60-80% is deionized water.

7. The coating composition comprising

(a) 10-40% of the epoxy ester graft acrylic polymer described in claim 1, including up to 5% neutralizing amines plus organic solvents, and 30-80% of deionized water,

(b) 0-40% of pigments and extenders,

(c) 0-20% of additives and/or reactive diluents, and

(d) 0-30% of a water soluble or dispersible crosslinker.

8. The coating composition of claim 7 wherein the epoxy ester graft acrylic polymer has at least 5-15% epoxy ester, 5-15% acrylic graft, up to 5% is neutralizing amine plus organic solvent, and 60-80% deionized water.

9. The coating composition of claim 7 wherein the additives are water soluble or dispersible linear or branched polyethylene oxides or polypropylene oxides with a $\overline{Mn}$ = 100-2500.

10. The coating composition of claim 7 wherein the water soluble or dispersible crosslinker is a methylated melamine formaldehyde resin.